Journal of Organometallic Chemistry, 136 (1977) C55—C56
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Preliminary communication

SYNTHESIS OF sym-POLYMETHYLCOBALTICENIUM SALTS

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Summary

The paper describes the synthesis of the series of sym-polymethylcobalticenium bromides and hexafluorophosphates of the general formula $[(Me_nC_5H_{5-n})_2Co]^+X^-$ ($X^- = PF_6^-$, Br^-).

The cyclopentadienyl ligands of the cobalticenium cation, unlike those of ferrocene, cannot undergo electrophilic substitution without changes in the type of the complex molecule. For that reason, only a rather small number of substituted cobalticenium salts is known. There is as yet no example of a series of cobalticenium compounds with a successively increasing number of substituents of a certain type. The present paper describes the synthesis of one such series.

An increase in the number of electron donor substituents rapidly decreases the acidity of alkylcyclopentadienes thus hindering direct substitution of sodium for hydrogen:

$$Alk_nC_5H_{6-n} + Na \rightarrow Alk_nC_5H_{5-n}Na$$

The exchange reaction with RNa ($R = C_4H_9$, C_5H_{11}) complicates the procedure. In order to obtain the organosodium derivatives, we used freshly prepared sodium amide in liquid ammonia. All homologues of the $(CH_3)_n$ - C_5H_{6-n} series readily undergo this reaction. Subsequent treatment of the reaction products with hexaamminocobalt(II) dichloride yields symmetrically substituted polymethylcobaltocenes. Oxidation of the latter leads to cobalticenium compounds, which can be isolated as salts containing various anions. For analytical purposes, poorly soluble hexafluorophosphates are particularly suitable.

The conditions applied in the reaction of alkylcyclopentadienylsodium derivatives with $[Co(NH_3)_6]Cl_2$, the yields and the physical constants of the products are listed in Table 1. The physico-chemical study of the compounds isolated is under way.

SYNTHESIS OF 8ym-Polymethylcodalticenium salts, [((CH3)nC3 H2-n), Co]*x TABLE I

Ligand Starting materials tions to $(OII_3)_n$ (OII_3), $(OII_3)_n$ ($OIII_3$), $(OIII_3)_n$ ($OIIII_3$), $(OIII_3)_n$ ($OIIII_3$), $(OIIII_3)_n$ ($OIIIII_3$), $(OIIII_3)_n$ ($OIIIII_3$), $(OIIIII_3)_n$ ($OIIIII_3$), $(OIIII_3)_n$ ($OIIII_3$), $(OIIII_3)_n$ ($OIIIII_3$), $(OIIII_3)_n$ ($OIIII_3$), $(OIIII_3)_n$ ($OIIIIII_3$), $(OIIII_3)_n$ ($OIIII_3$), $(OIIIII_3)_$				The state of the s						
(CH ₃) _n C ₂ H ₆ :n Na (FCo(NH ₃) ₆ ICl ₂ Tiff Temperation Time Yield Melting point (mol) (mol) (mol) (mil) ture (°C) (h) (%) X ⁻ m Br 0.025 0.026 0.01 65 55 55 4 73 186 (dec.) 0.030 0.026 0.013 56 60 4.5 77 212 (dec.) 0.055 0.020	Ligand (CII ₃) _n	Starting materi	elale		Reactle tions	on condi-		sym-Poli salts	rmethylcobalt	centum
0.025 0.026 0.01 65 55 3 80 214 (dec.) 0.020 0.025 0.01 55 55 4 73 185 (dec.) 0.030 0.026 0.013 56 60 4.5 77 212 (dec.) 0.055 0.050 0.020 80 60 4.5 70 210 (dec.)		(CII ₃) _n C ₅ H _{6:n} (mol)	Na (mol)	[Co(NH ₃) ₆]Cl ₂ (mol)	THF (m1)	Tempera- ture (°C)	Time (h)	Yield (%)	Melting poin	X = PF
0.020 0.025 0.01 55 55 4 73 186 (dec.) 0.030 0.026 0.013 56 60 4.5 77 212 (dec.) 0.055 0.050 0.020 80 60 4.5 70 210 (dec.)	CH, ⁰	0.025	0.026	0.01	55	56	9	08	214 (dec.)	260 (dec.)
0.030 0.026 0.013 55 60 4.5 77 212 (doc.) 0.055 0.050 0.020 80 60 4.5 70 210 (dcc.)	1,3-(CH,),	0.020	0.025	0.01	55	55	4	73	185 (dec.)	200 (dec.)
0.055 0.050 0.020 80 60 4,5 70 210 (dec.)	1,2,4-(CH ₃),	0.030	0,025	0.013	56	09	4.5	11	212 (doc.)	240 (dec.)
	(CII ₃),	0.055	0,050	0.020	80	09	4.5	20	210 (dec.)	219 (dec.)

a 1,1. Dinechylcobalticanium rhenate and tribromide were obtained as in [1]; the hexafluorophosphate salt is described in [2]; a mixture of mono- and 1,1'dimethyleobalticenium salts was obtained as in [3],

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